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Preparation of lanthanide nitrides by carbothermic reduction using ammonia

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Abstract

Some lanthanide dicarbides (CeC_2, PrC_2 and NdC_2) were prepared by the carbothermic reduction of their oxides (CeO_2, Pr_6O_{11} and Nd_2O_3) with carbon in vacuum at 1400°C. These carbides were converted into mononitrides (CeN, PrN and NdN) at 900°C under the gas flow of NH_3 or a mixture of gases (H_2:N_2 = 3:1). The nitrogen activity exhibited by NH_3 flow was calculated to be more than 1.0×10^3 and that of the mixture gas was 0.5. Since only mononitrides were obtained even when NH_3 with enormously high nitrogen activity was used, the higher nitride (e.g., sesquinitride or dinitride) seems not to exist in the Ce–N, Pr–N, Nd–N systems. The formation of CH_4 by the reaction of free carbon with the gas is found to depend on the hydrogen activity and carbon activity. © 1997 Elsevier Science B.V.

1. Introduction

Data on the formation and the stability of lanthanide nitrides are necessary in understanding the chemical behavior of lanthanide elements in UN fuel which has not been well characterized yet so far. As the first step for understanding the phase stability, we started with preparing pure lanthanide nitrides, which is the main purpose of this work. Another purpose is to ascertain whether the nitride higher than the mononitride (e.g., sesquinitride or dinitride) exists or not in the Ce–N, Pr–N and Nd–N systems.

Since Matignon [1] discovered lanthanide mononitrides, several researchers have carried out the studies on the lanthanide–nitrogen system. It is known that lanthanide mononitride can be prepared by the reaction of lanthanide metal or lanthanide hydride with nitrogen or ammonia at temperatures around the melting point of lanthanide metal or higher. Kieffer et al. [2] obtained lanthanide mononitrides by the reactions of cerium, praseodymium and neodymium with nitrogen and ammonia (1 bar pressure), at 1000–1100°C and 800–1100°C, respectively. Holleck et al. [3] prepared mononitrides of cerium and neodymium in nitrogen atmosphere above 1100 and 1550°C, respectively, while Gambino and Cuomo [4] obtained lanthanide nitrides in consolidated form by reactive arc melting in nitrogen atmosphere at 2000°C. About the preparation of lanthanide mononitride at a relatively low temperature, only Samsonov and Lyutaya reported the formation of cerium mononitride by the reaction of metallic cerium with a stream of ammonia above 200°C [5].

Among many fabrication methods of metal nitrides, the carbothermic reduction synthesis is a practical fabrication method in which the mixture of metal oxides and graphite or amorphous carbon is heat-treated in a stream of N_2/H_2 or NH_3 gas at high temperatures. This method in fact has been used to prepare uranium mononitride, but no report was found on the preparation of lanthanide nitride.

Ammonia has an excellent nitriding ability. The nitrogen activity, a_N, of a gas phase containing NH_3, N_2 and H_2 is represented by $a_N = (1/K_p)\{P(NH_3)/P(H_2)^{3/2}\}$, where $P(NH_3)$ and $P(H_2)$ are the partial pressures of ammonia and hydrogen, respectively, and K_p is the equilibrium constant for ammonia formation reaction: $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$. Under properly chosen conditions, the dissociation of NH_3 into N_2 and H_2 is suppressed to an extent. This equation for nitrogen activity indicates that the higher value of nitrogen activity is provided if the extent of dissociation of NH_3 is maintained lower than the equilibrium dissociation degree.

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2. Experimental

2.1. Materials

Lanthanide oxides used in this work were cerium oxide powder (CeO_2), praseodymium oxide powder (Pr_6O_{11}) and neodymium oxide powder (Nd_2O_3) with respective nominal purities of 99.999%, 99.999% and 99.999%. Powdered graphite and powdered amorphous carbon (non-graphitic carbon) (E. Merck AG, Darmstadt, Germany) were also used. Gas materials, NH_3 (99.998%), N_2 (99.999%), H_2 (99.999%) and Ar (99.99%) were fed from the commercial gas cylinders into apparatus through stainless steel capillaries without any further purification.

2.2. Apparatus

Two types of experimental apparatus, type I and type II, were used in this work. Type I was used in the carbothermic reduction at 1400°C and type II was used in the reaction of lanthanide carbide prepared in type I with an NH_3 stream or a $75\%H_2 + 25\%N_2$ stream at 900°C.

Apparatus type I consisted of a rotary pump, an oil diffusion pump and a sintering furnace. The type II apparatus consisted of the same kinds of pumps, a gas supply system and a gas analysis system. Both systems could be evacuated up to 10^{-6} Pa. A capacitance manometer (MKS Varatron type 122A, MKS Japan) was used to measure the total pressure in the range from 10^{-2} to 10^{2} kPa. The gas analysis system for measuring the partial pressures of NH_3 and N_2 consisted of a gas chromatograph (type GC-8APT, Shimadzu&Co., Kyoto, Japan), an integrator (type C-R6A, Shimadzu&Co., Kyoto, Japan) and a gas sampler with two sampling cocks. Helium gas of 99.999% purity was used as a carrier gas. The furnace temperature was controlled by an on–off type thermoregulator with a thermocouple mounted on the center of the outer surface of the reaction tube. Temperature of the specimen was determined with another thermocouple.

An X-ray diffraction pattern of reaction product was obtained at room temperature with a diffractometer (Rigaku Denki; Geiger flex rad-rA) using crystal-monochromatized Cu Kα radiation.

2.3. Procedure

Lanthanide oxide (CeO_2, Pr_6O_{11} and Nd_2O_3) powder and graphite or amorphous carbon powder were thoroughly mixed, in the desired proportion, in an agate mortar and pestle. Then polyvinyl alcohol was added as a binder and the powder was compacted into green pellets of 10.2 mm in diameter and 1.6 mm in height under a pressure of about 250 MPa. The weight ratio of carbon to lanthanide oxide as a starting material was determined assuming that lanthanide dicarbide and CO might be formed.

Three pellets were placed in a molybdenum boat and heated up to 1400°C in a vacuum furnace to convert oxides to carbides. After the heat-treatment, the furnace was cooled to room temperature and Ar gas was introduced to prevent the oxidation of the samples. A pellet was subjected to the X-ray diffraction measurement in order to identify the lanthanide dicarbides and other phases (e.g., M_2C_3, MO_2 and C). The other two pellets were taken for the reaction with an NH_3 stream or a $75\%H_2 + 25\%N_2$ stream in the type II apparatus. A quartz boat containing carbides was placed in the center of a quartz reaction tube. After the atmosphere was changed from N_2 to an NH_3 stream or a $75\%H_2 + 25\%N_2$ stream, the temperature was raised up to 900°C. Using the capacitance manometer and a gas chromatograph, the total pressure, $P(\text{total})$, and the partial pressures of N_2 and NH_3, $P(N_2)$ and $P(NH_3)$, were measured and $P(H_2)$ was calculated by the relation $P(H_2) = P(\text{total}) - P(N_2) - P(NH_3)$. After the end of each run, the reaction tube was quenched to room temperature. A part of the product was leached in 10 N HNO_3 solution to dissolve CeN, PrN and NdN and solutions were filtered off through a glass-filter to check whether insoluble residue (free carbon) was present or not. The other product was pulverized and embedded in a sample holder with an epoxy resin to avoid possible oxidation of the specimen during X-ray diffraction. The above sample preparation was done under an Ar atmosphere.

3. Results and discussion

The conditions and results of the carbothermic reduction experiments are summarized in Table 1. The X-ray diffraction patterns of the reaction products of CeO_2 with graphite or amorphous carbon (runs 1 and 2) are shown in Fig. 1(a) and (b), respectively, indicating that the major solid phase is CeC_2. The formations of PrC_2 and NdC_2 (runs 3 and 4) were also verified. The crystal structures of these rare earth dicarbides are face centered tetragonal. The conditions and results of the nitridation experiments are summarized in Table 2. The X-ray diffraction pattern of run 5 shows the presence of CeN and graphite (see Fig. 1(c)). On the other hand, in the reaction product of run 6,

Table 1
Conditions and results of carbothermic reduction experiments

Run	Starting materials [a]	Product	Lattice constant (Å) [b]
1	$CeO_2 + C(G)$	CeC_2	$a = 5.489$, $c = 6.484$
2	$CeO_2 + C(A)$	CeC_2	$a = 5.491$, $c = 6.495$
3	$Pr_6O_{11} + C(A)$	PrC_2	$a = 5.454$, $c = 6.441$
4	$Nd_2O_3 + C(A)$	NdC_2	$a = 5.411$, $c = 6.410$

[a] C(G) and C(A) stand for graphite and amorphous carbon, respectively.

[b] Crystal structure: face centered tetragonal, temperature: 1400°C, time: 12 h.

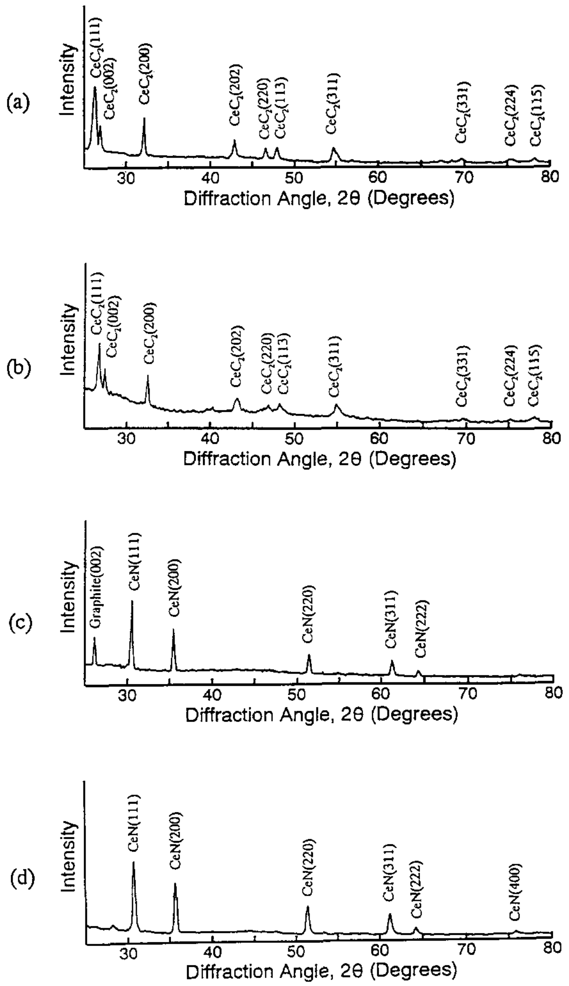

Fig. 1. X-ray diffraction patterns of the reaction products of (a) CeO_2 with graphite, (b) CeO_2 with amorphous carbon, (c) CeC_2 containing graphite with an NH_3 stream and (d) CeC_2 containing amorphous carbon with an NH_3 stream.

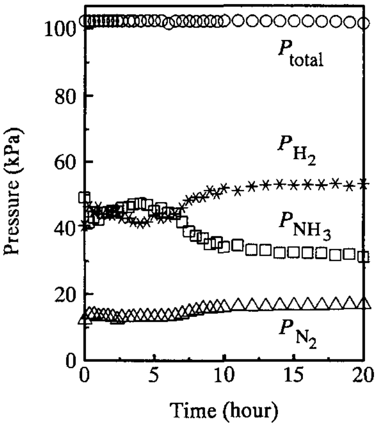

Fig. 2. Variation of P_{total}, $P(H_2)$, $P(NH_3)$ and $P(N_2)$ with time during run 8.

the solid phase consists only of CeN (see Fig. 1(d)). In comparing the diffraction patterns of run 5 and run 6 shown in Fig. 1(c) and (d), an obvious difference should be noted. A peak due to graphite around 26° was observed only in run 5. This difference indicates that the removal efficiency of free carbon depends on the kind of carbon (graphite or amorphous carbon) as the starting material. The graphite is difficult to be removed even by NH_3 stream.

Katsura [6] derived nitrogen and hydrogen activities, a_N and a_H, $a_N = (1/K_p)P(NH_3)/P(H_2)^{3/2}$ and $a_H = \{(1/K_p)P(NH_3)/P(N_2)^{1/2}\}^{1/3}$, respectively, where $P(NH_3)$, $P(N_2)$ and $P(H_2)$ are the partial pressures of NH_3, N_2 and H_2 and K_p is the equilibrium constant of $\frac{1}{2}N_2 + \frac{3}{2}H_2 = NH_3$. The values of nitrogen activity, a_N, calculated at the end of each run using this equation are also given in Table 2, suggesting that very high a_N values have been obtained by use of an NH_3 stream compared to a_N values of a $75\%H_2 + 25\%N_2$ stream. In runs 9 to 12,

Table 2
Conditions and results of nitridation

Run	Specimen	Reaction gas (flow)	Time (h)	Product	Nitrogen activity	Hydrogen activity	Lattice constant (Å) [a]
5	CeC_2(G) [b]	NH_3	45	CeN + C	1.61×10^3	11.7	5.024
6	CeC_2(A) [c]	NH_3	20	CeN	3.01×10^3	14.3	5.026
7	PrC_2(A) [c]	NH_3	20	PrN	3.04×10^3	14.5	5.169
8	NdC_2(A) [c]	NH_3	20	NdN	3.69×10^3	15.1	5.169
9	CeC_2(G) [b]	$75\%H_2 + 25\%N_2$	45	CeN + C	0.5	0.87	5.026
10	CeC_2(A) [c]	$75\%H_2 + 25\%N_2$	20	CeN + C	0.5	0.87	5.027
11	PrC_2(A) [b]	$75\%H_2 + 25\%N_2$	20	PrN + C	0.5	0.87	5.166
12	NdC_2(A) [c]	$75\%H_2 + 25\%N_2$	20	NdN + C	0.5	0.87	5.176

Temperature: 900°C.
[a] Crystal structure: face centered cubic.
[b] (G): graphite was used as the starting material.
[c] (A): amorphous carbon was used as the starting material.

where a $75\%H_2 + 25\%N_2$ stream were used, the free carbon was found to remain together with mononitride. At 900°C H_2 reacted with even amorphous carbon much more slowly than NH_3. These facts indicates that graphite carbon ($a_C = 1$) hardly reacts with reactant gases to generate CH_4 and CH_4 is formed only by the combination of NH_3 and amorphous carbon.

Fig. 2 shows the time variation of P(total), $P(H_2)$, $P(NH_3)$ and $P(N_2)$ of run 8. Some irregular variations of $P(H_2)$ and $P(NH_3)$ were observed for 10 h and then a stationary state is reached where there is no appreciable time dependence of $P(H_2)$, $P(NH_3)$ and $P(N_2)$. This figure indicates that the reaction of NdC_2 with an NH_3 stream was almost completed within 10 h.

4. Conclusions

Lanthanide dicarbides (CeC_2, PrC_2 and NdC_2) were prepared at 1400°C by the carbothermic reduction of the mixtures of lanthanide oxides (CeO_2, Pr_6O_{11} and Nd_2O_3) and carbon (graphite or amorphous carbon).

Lanthanide mononitrides (CeN, PrN and NdN) were prepared by the reaction of lanthanide dicarbides with an NH_3 stream and a $75\%H_2 + 25\%N_2$ stream at 900°C.

Only the combination of an NH_3 stream and amorphous carbon can form CH_4 probably because of high a_H and a_C values.

The nitride higher than the mononitride (e.g., sesquinitride or dinitride) seems not to exist in the Ce–N, Pr–N and Nd–N systems, since only mononitrides were obtained even when NH_3 with enormously high nitrogen activity was used.

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